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# COMPOSITION AND THERMAL PROPERTIES OF MAGNESIUM BORIDES

Markovskii, I. Ya, et al

The first mention of magnesium borides occurs in the work of A. Gester who obtained them from sodium fluoroborate and magnesium metal. Later the product, to which a formula  $Mg_2B_3$  was assigned, was obtained by F. Jones<sup>2</sup> and R. Taylor<sup>3</sup> from the action of magnesium on boric oxide, from boron and magnesium and boron trichloride and magnesium. Their results were confirmed in 1895 by Moissan in his studies of possible methods of preparation of elemental boron<sup>4</sup>. However, Moissan notes that besides the boride that is easily decomposed by water and dilute mineral acids consequent liberation of volatile hydrides of boron, there also exist another boride of magnesium which is not affected by even a prolonged treatment with acids. This other boride of magnesium is one of the most difficultly removable impurities from the amorphous boron and, according to Moissan<sup>4,5</sup> could be removed by fusion with excess boric oxide.

In 1914, R. Ray<sup>6</sup> confirmed the composition of magnesium boride to be  $Mg_2B_3$  and further were stated that no other boride of magnesium exists. This point of view became universally acceptable particularly after the work of Stock and his coworkers<sup>6,7</sup> pertaining to the study of magnesium boride, its properties and its possible use as a raw material for preparation of hydrides of boron<sup>8,9,10</sup>. However in the earlier work of W. Travers and R. Ray<sup>11</sup> there exist data which contradict the then accepted composition of magnesium boride ( $Mg_2B_3$ ). Their study of hydrolysis products of magnesium boride did not correspond to the  $Mg_2B_3$  formulation and they proposed the existence of the  $Mg_2B_4$  boride. Up to some fairly recent publications<sup>12,13</sup> pertaining to the structure of magnesium diboride, and confirming the work of the authors, there was no physico-chemical data available in the literature concerning borides of magnesium.

The purpose of this investigation was the study of the system Mg-B and properties of the individual compounds formed in this system. The difficulties associated with the study of the system, such as volatility of magnesium metal, impossibility of obtaining monocrystals (single crystals) of the binary components that were found, as well as certain complications of analytical nature leading the lack of certainty of differentiating between free and combined boron, have so far not allowed to completely establish the composition and structure of solid phases containing high percentage of boron. In case of magnesium diboride, however, the data obtained are completely reliable.

## Experimental

Various boride compositions were prepared from amorphous boron and powdered magnesium. The amorphous boron was found to contain 96 percent boron, 1.4 percent magnesium, 1.1 percent aluminum and iron and 0.3 percent silicon. Magnesium metal

used had the following impurities: 0.1 percent aluminum, 0.07 percent iron and 0.05 percent silicon.

The powder elemental components were thoroughly mixed in an agate mortar in a desired ratio and then transferred to a graphite crucible (container) in which the mixture was then either pressed by hand or was briquetted at 800 Kg/cm<sup>2</sup> pressure. The heating process was then carried out as follows: The graphite crucibles were placed either in iron or quartz reaction vessels in the atmosphere of carefully purified hydrogen and were then hermetically sealed. Preliminary degassing was accomplished by heating at 150°C in hydrogen atmosphere. The hermetically sealed reactors were then heated in a muffle furnace to a desired temperature and maintained at that temperature for a desired period of time, after which they were rapidly cooled in cold water. The actual reaction temperature was measured by means of Pt-Pt/Rh thermocouple inserted into the reaction vessel. Due to the exothermal nature of reaction between boron and magnesium, the start of reaction could always be noted by a sudden jump in the temperature readings.

Preliminary chemical and x-ray analyses showed the absence of possible reaction between graphite crucible and the components of the reaction charge.

The various reaction masses obtained for a series of Mg/B ratios varied in color from dark brown to black. These products were subjected to both chemical and x-ray analysis.

The x-ray analysis was conducted with FeK<sub>α</sub> source in a 57.3 mm coll. The most typical samples were further analyzed in a 143.2 mm coll.

Chemical analyses were carried out separately on nitric acid soluble and the insoluble fractions. The nitric acid digestions were made in sealed glass tubes at 150°C for 48 hours in order to avoid possible losses of volatile boron hydrides. The insoluble residues were then further analyzed by the standard sodium carbonate fusion method. A small amount of sodium nitrate was also used in these fusions. Boron was determined by standard volumetric methods - titration with .1N Ba(OH)<sub>2</sub> in presence of mannitol. Magnesium was determined (after H<sub>2</sub>SO<sub>4</sub> removal with methanol) as pyrophosphate. Uncombined magnesium was determined by vacuum distillation at 450°C.

Specific gravities were determined on carefully ground up samples (-100μ) pycnometrically in benzene.

#### Phase Analysis of Reaction Products Between Magnesium and Boron

The x-ray analyses of reaction products of interaction of boron and magnesium in the following range of Mg/B mol ratios 2:1, 3:2, 1:1, 1:2, 1:4, 1:6, and in the temperature range of 800-1200°C show that phase composition of reaction products in the two hour heating tests (Table I) depends almost exclusively on the reaction temperature and not on the reaction charge composition.

A noticeable reaction between magnesium and boron starts in the 720 ± 20°C temperature region; at these low temperatures the only solid phase obtained is MgB<sub>2</sub>. At higher reaction temperatures other solid phases begin to appear. These were numbered alphabetically A, B, C and are in general characterized by their progressively

higher boron content than that obtained with thermal decomposition of  $MgB_2$ , as seen from the data in Table 2.

TABLE 1

Phase Composition of Reaction Products Between Magnesium and Boron

Mg/B mole Ratio	Reaction Temperature	Phase Composition Based on X-Ray Analysis Data
2:1	800	$MgB_2$ + excess free Mg
3:2	800	A + B
1:1	1140	$MgB_2$ + free Mg
3:4	800	$MgB_2$ + free Mg
	800	Free Mg + traces of $MgB_2$
	600	$MgB_2$ + free Mg
	700	$MgB_2$
	800	$MgB_2$
1:2	950	A + $MgB_2$
	1000	A + traces of $MgB_2$
	1050	A + B
	1200	C
1:4	900	A
	1000	A
	1050	A
	1200	C
1:6	800	$MgB_2$ + free boron
	1000	A
	1200	C

TABLE 2

Phase Composition of Thermal Decomposition Products of  $MgB_2$ 

Heating Temp.	Length of Heating (hr.)	Percent $HNO_3$ Insoluble in Product	Phase Composition Based on x-ray Analysis Data
800	2	6.2	$MgB_2$
900	4	24.5	$MgB_2$ + traces of boride A
1000	2	81.3	Boride A + Traces of $MgB_2$
1140	2	86.1	Mixture of boride A + B
1200	2	92.6	Boride C
1300	2	-	Boride C
1400	2	-	Boride C
1500	4	-	Boride C
	(in vacuum)		

Phase composition of the reaction products is characterized by x-ray diagrams, shown in Figure 1. The data from Table 2 indicate unusually high stability of magnesium boride phase B, about which more will be said later in this article.

#### Boride Composition $MgB_2$

Magnesium diboride is a dark brown powder, specific gravity of which 20°C varies from 2.48 to 2.67 depending on the amount of nitric acid insoluble residues present in sample. Water decomposes it slowly, while mineral acid decomposition of magnesium diboride may become violent. Volatile hydrides of boron are evolved during hydrolysis of magnesium diboride. Thus, treatment of it with hot hydrochloric acid leads to complete solution. During this treatment 0.8 to 1.1 percent of total boron is released as volatile hydrides. Concurrently about 2 moles of hydrogen per mole of  $MgB_2$  are evolved (experimental data show 2.11 to 2.12 moles of  $H_2$  evolved). This is in agreement with data of Traverse and Bayl<sup>11</sup>. This is the basis of the hydrolysis equation proposed by the above mentioned investigators:



Magnesium diboride is the product of the relatively low temperature interaction of magnesium and boron. Thus traces of it are found by x-ray analysis in magnesium-boron mixtures heated to 600°C. The most favorable temperature for its formation is in the 800°C range, and it is desirable to have excess magnesium present in the reaction mixtures to compensate for the volatility of magnesium. Bridgman of the reaction charges seems to help in decreasing the loss of magnesium.

In the 800°C temperature range it is possible to obtain the magnesium diboride product containing 2-5 percent of nitric acid insolubles consisting of unreacted boron and mixtures of other insoluble borides.

The upper temperature limit of stability of magnesium diboride was found to be below 1050°C, since in the samples that were heated at that temperature there was no  $MgB_2$  found by x-ray analysis.

The data in Table 1 also show that, with reaction mixtures of higher than 1:2 Mg to B ratios, only  $MgB_2$  with excess free magnesium is obtained, and consequently no other magnesium boride, containing more than 1 atom of magnesium and two atoms of boron, should exist. This is further confirmed in Table 3 which lists data on vacuum removal of excess magnesium from reacted masses obtained at 800°C. The  $MgB_2$  lines (on x-ray powder photographs) are also seen on the sample of magnesium boride synthesized by the method of Steck<sup>6,7</sup>, which turned out to be a mixture of magnesium diboride and metallic magnesium.

The chemical composition of the magnesium diboride phase is shown by chemical analysis in Table 4. Theoretical composition of  $MgB_2$  is 53% Mg and 47% B.

X-Ray Powder Photographs of Various Magnesium Boride Phases (1) MgB<sub>2</sub>,  
(2) Phase A, (3) Phase B, (4) Phase C



Results of Test on Vacuum Distillation of Uncombined Magnesium from Magnesium Boride Products of Various Compositions

Test No.	Reaction Mass Mg:B mol/ratio	Per cent Mg Distilled from Boride Product	Theoretical Excess Mg	Phase Composition of Product
1	1:1	32.4	34.6	Phase A Phase B Phase C Magnesium
2	3:4	25.7	26.5	
3	3:2	52.8	51.5	
4	Boride made by method of Stock Mg + B <sub>2</sub> O <sub>3</sub>	-	-	
5	1:2	0.0	0.0	

TABLE A

Chemical Analysis of Magnesium Diboride Samples

Test No.	B <sub>2</sub> O <sub>3</sub> Anal. %	Composition Percent Mg	% Mg	% Mg + % B
6	1.5	51.5	47.2	32.0
7	5.2	51.5	45.8	51.6
8	6.2	51.5	43.2	53.9
9	6.0	51.5	41.6	54.1

The structure of magnesium diboride was determined from x-ray powder photographs and is characterized by the following data:

Hexagonal system,  $a = 3.512 \pm 0.001$  Å,  $c = 3.512 \pm 0.001$  Å,  $c/a = 1.141$ , or in Angstrom units  $a = 3.512$  Å, space group  $D_{12h}^6$ ,  $C_6/mmm$ , number of molecules in a crystal nucleus  $1.6 \times 10^{23}$  g/cm<sup>3</sup>. Structure is of the same type as  $AlB_2$  and is composed of trigonal prisms of Mg atoms with the B atom in the center. Mg(000), B ( $1/3 \ 2/3 \ 1/2$ ), B ( $2/3 \ 1/3 \ 1/2$ ) in the center. Mg(000), B ( $1/3 \ 2/3 \ 1/2$ ), B ( $2/3 \ 1/3 \ 1/2$ )

Distances between the two Mg atoms of the same layer 3.03 Å, between the Mg atoms with neighboring layers 3.52 Å. The Mg-B distance is equal to 2.50 Å and the B-B distance is 1.78 Å.

Good agreement between the experimental and calculated interplanar distances and intensities of lines (in powder photographs), Table 5, demonstrates the validity of the structure of magnesium diboride. These results also agree well with the data of other investigations<sup>12,13</sup>.

TABLE 5  
Experimental and Calculated Interplanar Distances and Line Intensities of X-ray Powder Photographs on  $MgB_2$

hkl	d/a obs (in Å)	d/a calc (in Å)	I obs	I calc	hkl	d/a obs (in Å)	d/a calc (in Å)	I obs	I calc
001	3.53	3.512	5	8	200	1.334	1.333	5	4
100	2.668	2.667	25	29	201	1.2462	1.2465	20	20
101	2.122	2.124	100	100	003	-	1.1707	0	1
002	1.756	1.756	10	13	112	1.1574	1.1577	25	31
110	1.539	1.539	30	24	103	1.0718	1.0719	15	24
102	1.466	1.467	10	10	202	1.0619	1.0619	5	7
111	1.409	1.410	5	3	120	1.0076	1.0079	10	17

Thus, magnesium diboride belongs in the rather extensive group of diborides of other metals<sup>14</sup>, and in particular of transition group metals Cr, Ti, Nb, Ta, V, Cr, Mo, W which have similar to Mg values of atomic radii (ratio  $r_{B_2}/r_{Mg}$  in the 0.56-0.66 range). It is necessary, however to note, a high degree of chemical activity for  $MgB_2$  as compared to the diborides of the above mentioned metals and also including aluminum diboride, all of which possess a high degree of inertness (with the exception of  $ZrB_2$  which also is decomposed by HCl hydrolysis with liberation of volatile hydrides of boron<sup>15</sup>).

Acid Insoluble Magnesium Borides

With the help of x-ray powder photographs, three acid insoluble magnesium boride phases were found, which differ from the above discussed  $MgB_2$  in that, even upon prolonged digestion in conc. HCl, no change in weight or composition is observable in these borides. Usually these insoluble boride phases are obtained as mixtures with other boride phases. Thus, boride phase A, if it is obtained at reaction temperatures of less than  $1050^\circ\text{C}$  is obtained mixed with  $MgB_2$  phase; boride phase B is often obtained mixed with boride phase A. Only boride phase C is obtained free of other, already mentioned, boride phases; it is however found to be mixed with free boron. Due to complex nature of the x-ray powder photographs obtained on these acid insoluble magnesium borides, and further more due to absence of monocrystal specimens, the structure of these phases were not elucidated.

Chemical composition of these higher borides is also somewhat inconclusive due to probable presence in samples of these borides of free boron which is analytically impossible to determine separately from the combined boron, and the presence of which could only be surmised from the x-ray powder photographs. However, the existence of the three above mentioned magnesium boride solid phases A, B and C has been established by numerous x-ray powder photographical analyses on samples of borides produced by direct synthesis from the elements at desired temperatures, as well as of identical boride solid phases obtained by thermal decomposition of magnesium diboride or of the solid phase A (Figure 1).

Magnesium Boride Phase A.

The temperature region of the existence of this phase lies between  $900.$  and  $1150^\circ\text{C}$ . This phase after its separation from the magnesium diboride (by digestion with HCl) is isolated as a dark brown powder with  $d_{50} 2.45\mu$ . The x-ray powder photograph data for the phase A are listed in Table 6.

TABLE 6

Interplanar Distances and Intensities of X-ray Powder Photographs of Magnesium Boride Phase A.

$d/\text{\AA}$ in KX	Intensity	$d/\text{\AA}$ in KX	Intensity	$d/\text{\AA}$ in KX	Intensity	$d/\text{\AA}$ in KX	Intensity
4.17	very weak	1.89	weak	1.389	weak	1.158	weak
3.78	weak	1.86	medium	1.345	very weak	1.144	medium
3.08	weak	1.83	medium	1.321	bright	1.125	weak
2.72	weak	1.76	weak	1.310	bright	1.098	medium
2.52	very bright	1.71	weak	1.300	weak	1.081	medium
2.32	bright	1.69	weak	1.270	weak	1.068	bright
2.26	medium	1.63	bright	1.260	weak	1.061	weak
2.20	bright	1.60	very weak	1.253	weak	1.048	bright
2.16	medium	1.58	weak	1.219	weak	1.045	medium
2.05	very weak	1.53	bright	1.203	very weak	1.026	bright
2.01	medium	1.451	medium	1.166	medium	1.016	weak
1.96	bright	1.420	medium				

Magnesium content in individual samples of the magnesium boride phase A varies from 19 to 32.5 percent (see Table 7), and it has to be noted that in some x-ray powder photographs of the magnesium boride phase A there appear elemental boron lines. This latter case as well as the fact that the higher magnesium content of magnesium boride phase A samples is obtained from reaction charge compositions containing excess magnesium, allows to assume that phase A corresponds to the  $MgB_2$  composition (Theoretical content- 27.2% Mg, 72.8%B). The low magnesium content of some of the phase A samples can be explained by a somewhat low thermal stability of this boride phase with the resulting loss of volatile magnesium and liberation of the excess elemental boron.

TABLE 7

Synthetic Preparation of Magnesium Boride Phase A

Sample No.	Mg/B mole ratios in reaction charge	Reaction (heating) temp.	Heating Time (hours)	Mg content (percent) in acid insoluble fraction of Product	Phase composition of product	Remarks
1	Thermal decomposition of $MgB_2$	1000	3	32.5	A	Bridged charges
2	1:4	1000	2.5	24.5		
3	1:4	1050	2	24.0		
4	1:4	1050	2	21.9		
5	1:4	1080	0.5	27.6	A + free boron	
6	1:6	1040	2	18.8		
7	1:6	1080	3	19.4		
8	1:4	1060	2	23.1	A	
9	1:4	1140	3	27.8		
10	1:6	1120	3	24.0		
11	1:6	1090	3	22.3		

On the other hand, the fact that phase A corresponds to  $MgB_2$  composition and not the  $MgB_4$ , as Russell, Hirst, Kanda and King<sup>12</sup> contend, is substantiated first by complete analyses of the most representative phase A samples, even those obtained from the Mg:B mole ratios of 1:4, as shown in Table 8, and second by the observed evolution of excess magnesium metal from these mixes as compared to tests performed with the Mg:B mole ratio of 1:6 mixes.

TABLE 8

Analyses of the Most Representative Samples of Magnesium Boride Phase A

Test No.	Percent Composition				Percentage sum of Phase Components
	Mg	B	Si	Fe + Al	
8	23.1	73.6	0.2	1.4	98.3
5	27.6	69.6	0.2	0.8	98.0



Moreover, in special tests I-11 (see Table 7) which were carried out in a hydrogen atmosphere, in hermetically sealed steel bombs, that is under conditions insuring against the loss of magnesium, the acid insoluble fraction of the magnesium boride product was found to have either a practically theoretical (97.15%) content of magnesium for the  $MgB_2$  composition or a somewhat lower one; on the basis of the above mentioned data it can be stated with assurance that the boride phase A corresponds to  $MgB_2$  composition.

It can also be added that the  $MgB_2$  boride, if heated with concentrated nitric acid is completely changed to the magnesium diboride ( $MgB_2$ ). The boride was found to be relatively stable to a prolonged digestion with 1:1 HCl. Thus, after 24 hour boiling in 1:1 HCl only 0.19 percent of boron was found in solution. Hydrogen peroxide and nitric acid also were found to act very slowly on the boride.

#### Magnesium Boride Phase B.

The boride phase B gives x-ray powder photographs that are quite different from those of phase A (Table 9) and thus could be considered as a new mixture, contained in phase A, but must be considered as a separate phase. However the temperature range of its stability is much narrower than that of phase A. Magnesium boride phase B is a dark brown powder with a density  $d_{20} = 2.47$ . This phase is obtained in the 1100-1200°C range. Above 1500°C it decomposes with the formation of magnesium and boron. On the basis of the most representative samples of magnesium boride phase B, x-ray powder photograph analysis to contain no boride phase A, and the results of the analysis found difficult to assign any definite chemical composition to this phase on the basis of available analytical data.

#### Magnesium Boride Phase C.

This magnesium boride phase is hermetically stable up to 1500°C. According to the data in Table 2, this phase is quite stable even at 1500°C in vacuum. This fact points to the individuality of this phase. The samples of this magnesium boride phase C are dark brown in color with a density  $d_{20} = 2.44$ . Only above the temperature of 1700°C it is noticeably changed. Above 1700°C it decomposes into free boron and magnesium, which then dissolves in acid. Magnesium boride phase C is only obtained at temperatures above 1500°C, the composition is independent of the reaction charge composition. It is also stable to the decomposition of the  $MgB_2$  and  $MgB_3$  phases. The composition of this phase, according to data in Table 11, is very close to the  $MgB_{1.2}$  formula (theoretical  $MgB_{1.2}$  is 84.9% B).

TABLE 9

Interplanar Distances and Intensities of X-ray Powder Photographs of Phase B

d/a (Å)	I	d/a (Å)	I	d/a (Å)	I
7.27	weak	2.52	very weak	1.68	weak
6.43	medium	2.42	bright	1.60	weak
3.55	medium	2.32	medium	1.415	weak
3.38	medium	2.18	bright	1.284	weak
3.22	weak	1.78	weak	1.254	very weak
2.71	medium	1.75	weak	1.224	very weak

TABLE 10

Data Pertaining to Magnesium Boride Phase B

Test No.	Method of Preparation	Composition %				Summation Percentage %	Phase Composition
		Mg	B	Si	Fe + Al		
1	Thermal decomposition of $MgB_2$ at 1100°C for 3 hours	19.4	76.0	0.1	0.6	96.1	Phase B
2	Thermal decomposition of $MgB_2$ at 1150°C for 5 hours	19.8	76.7	0.5	0.7	97.7	Phase B well formed
3	Thermal decomposition of $MgB_2$ at 1200°C for 3 hours	14.0	80.1	0.4	0.7	95.2	Phase B plus some phase C
4	From elements Mg:B ratio 1:2 at 1050°C for 3 hours	23.0	-	-	-	-	Phase A + Phase B
5	Thermal decomposition of $MgB_2$ at 1200°C for 3 hours	19.8	-	-	-	-	Phase B

11.

TABLE 11  
Data for the Magnesium Boride Phase C.

Test No.	Conditions for Boride Formation	Composition (Percent)		Phase Composition	Remarks
		Mg	B		
1	Synthesis from the Mg:B mol/ratio 1:1 at 1800°C, 2.5 hrs	15.4	82.0	Sharp G <sub>1</sub> peak B lines on x-ray photograph	Estimated G <sub>1</sub> peak
2	Thermal decomposition of MgB <sub>2</sub> at 1850°C for 1 hour	12.7	82.0	Phase G	
3	Thermal decomposition of MgB <sub>2</sub> at 1850°C for 1 hour	14.8	83.5		
4		15.0	81.5	Phase B and perhaps some free boron	
5	Thermal decomposition at 1900°C for 1 hour	15.6	81.6		
6	same at 1800	15.0	81.6		
7	same at 1900	15.0	80.9		
8	same at 1800	14.8	81.4		
9	same at 1870	13.8	83.3	Phase of free boron	
10	same at 1700	0.9	96.6		
11	same at 1900	0.4	97.8		

TABLE 12  
Extinction Distances and Intensity Lines of Phase B

Wavelength (Å)	Intensity	1/A (cm <sup>-1</sup> )	Intensity	1/A (cm <sup>-1</sup> )
2.40	weak	2.16	weak	1.68
2.42	medium	2.05	medium	1.61
2.44	medium	1.95	medium	1.57
2.46	weak	1.84	medium	1.50
2.48	bright	1.77	bright	1.38
2.50	medium	1.55	very weak	1.27

All the samples of this magnesium boride phase B, which are partially reduced, are shown in Figure 2 and Table 12) which are partially reduced. The samples of boron obtained by reduction of boron trioxide (B<sub>2</sub>O<sub>3</sub>) at the present sample of boron), and are entirely identical with the photographs of "true" Reichen boron. In some of these x-ray powder photographs only one extremely line is seen, which is undoubtedly due to some impurity. The x-ray powder photograph data obtained show that magnesium boride is identical

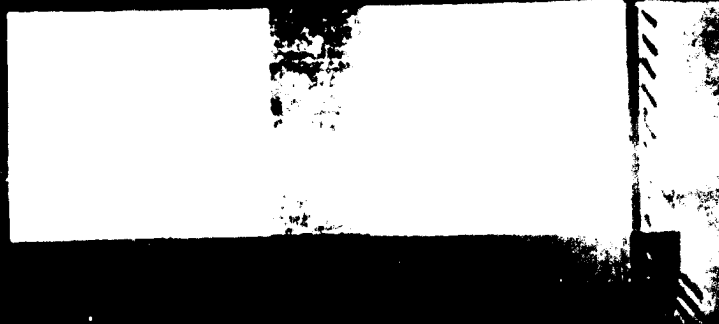
12.

to the hard to get rid of impurity in elemental boron as described by Moissan's. This same phase C is also identified on x-ray powder photographs of the purified boron samples produced by the Moissan (magnesium-thermic) method.

It is highly probable that the chemical composition of magnesium boride phase C corresponds to the  $MgB_{12}$  formula. It has to be noted, however, that the possibility of free boron in this phase has not been excluded.

FIGURE 2

X-Ray Powder Photographs of Magnesium Boride Phase C Obtained Under Various Conditions - (1) at 1200°C, (2) at 1300°C, (3) at 1500°C, (4) at 1600°C, (5) boron obtained from  $B_2O_3 + H_2$ , (6) raw Moissan boron



Magnesium boride phase C is very stable toward the action of mineral acids. Thus a sample of it, boiled for 100 hours in 1:1 HCl showed no discernible change in the chemical analysis for magnesium and for boron before and after the treatment. Hydrogen peroxide or nitric acid decompose it very slowly even at boiling temperatures. For decomposition of this boride, the most acceptable method involves fusion with alkali carbonates or hydroxides.

#### Probable Mechanism for Magnesium-Thermic Reduction of Boric Oxide

Moissan's method for production of amorphous boron involves a reaction between boric oxide, taken on a theoretical basis of theory, and metallic magnesium, preferably in an inert atmosphere. Reduction of boric oxide is desirable for two reasons: first it provides a gas phase at reaction temperatures and protects the

heated reaction products from contact with air, second it helps decompose various magnesium borides that are obtained as by products.

The primary product of the magnesiothermic reduction of boric oxide, as seen from the tests involving reaction of boric oxide and excess magnesium for the purpose of producing magnesium borides, is magnesium diboride  $MgB_2$  (see Table 3).

The magnesium diboride is obtained from the highly exothermic reaction:



The exothermic character of the above reaction is due, actually to two separate exothermic reactions: one, the reduction of boric oxide by magnesium metal and two, the formation of magnesium diboride from the elements.

However, only traces of  $MgB_2$  is found in the reaction products when excess boric oxide is reduced by magnesium, while in the amorphous boron product, obtained after the acid digestion, the magnesium boride  $MgB_{1.2}$  lines are observed on x-ray powder photographs, it is therefore logical to assume that magnesium diboride reacts with excess boric oxide according to the following scheme:



In fact, the "raw" Moissan boron (that is the magnesiothermic reaction product subjected to a rapid acid digestion in order to dissolve excess  $B_2O_3$  and  $MgO$ ), according to literature data<sup>18</sup>, as well as to the chemical analysis, of the same order of magnitude as that appearing in the right side ( $MgB_{1.2} + 6B$ ) of the above equation.

This also is in accord with the already mentioned fact that the phase composition of "raw" boron, as seen from the x-ray powder photographs (number 6 in Figure 2) is almost identical with that of magnesium boride phase C and contains only a small amount of elemental boron.

Reaction between  $B_2O_3$  and  $MgB_2$ , probably, is either weakly exothermic, or slightly endothermic, and thus requires preliminary heating of the reaction mass. Stability of boride phase C in respect to acids explains the known difficulty of purifying the "raw" boron by means of the acid digestion methods. In fact, according to various literature sources, preparation of amorphous boron by the Moissan method of higher than 90-95 percent purity is a very difficult task<sup>19, 20</sup>.

Moissan has advocated using a 50 fold excess of boric oxide in melting the "raw" boron in order to decompose the magnesium boride impurity and thus raise the purity of the resulting amorphous boron to 98 percent.

The possibility is not entirely eliminated that in the highly exothermic reaction between boric oxide and magnesium, there may occur some thermal decomposition of magnesium diboride into the above discussed higher borides of magnesium. The short time interval of the actual high temperature reaction, however, does not allow to attribute too much influence of the thermal decomposition re-

<sup>18</sup>data, contains from 8 to 13 percent magnesium, that is the "raw" boron has the magnesium content

action product. The data Stock<sup>1</sup> however show that in order to obtain magnesium boride that is a good raw material for the hydrides of boron production, one has to select an optimum Mg B<sub>2</sub>O<sub>3</sub> ratio or else the high temperatures of reaction yield products that yield only traces of volatile hydrides of boron.

#### Conclusions:

- (1) As a result analysis of the system Mg-B the authors show four boride phases, a hexagonal phase MgB<sub>2</sub>, belonging to the structural type AlB<sub>2</sub>, and three other phases A, B and C, the structure of which has not as yet been determined.
- (2) Magnesium diboride was shown to be a relatively active material, yielding volatile hydrides of boron upon action of water or dilute mineral acids. Its thermal stability is not great, and at higher temperatures it dissociates into magnesium and boron, with liberation of free magnesium, into the other boride phases A, B and C.
- (3) The temperature regions of stability of these other magnesium boride phases have been established, as well as their chemical composition. In particular it was shown that phase A closely corresponds to MgB<sub>2</sub> composition, while phase C corresponds to MgB<sub>1.2</sub> composition.
- (4) Magnesium boride phase C is noted for its high chemical and thermal stability and does not dissociate appreciably until the temperature of about 1800°C is reached. This boride phase C was also found in all samples of magnesium boron prepared by the Moissan method.
- (5) A tentative reaction mechanism is offered concerning the magnesium-boron reduction of boric oxide.

#### Literature:

S.B.V. Bakresoff. Course in General Chemistry, Edition 10-a, 539 (1973)

Translated by  
V.V. Lovasheff  
Gim